THE CARBONATION OF WATER SOFTENING PLANT SLUDGE

By

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CHAPTER I

INTRODUCTION

The disposal of sludge produced by lime or lime-soda softenplants is becoming an increasing problem in the United States. This is true for three major reasons. First, there has developed a steadily increasing demand on the part of consumers for a supply of soft water. In the past five years, forty lime or lime-soda softening plants have been constructed in Florida alone, having a total capacity of approximately 160 million gallons per day. The second reason for the importance of softening sludge disposal is that the country has become more "pollution conscious." According to Waring, [1] the Ohio Water Pollution Board has declared water softening sludge a pollutant and requires permits for all plants discharging such wastes into lakes or streams. Other States have enacted similar laws. The third reason is the substantial increase in sludge volumes due to the increase of urban population. The volume of softening sludge produced by a lime or lime-soda softening plant is very large. For example, when the Hialeah Softening Plant of the City of Miami is operating at a rate of 60 million gallons per day, it produces approximately 135 tons per day of dry weight sludge suspended in approximately one-half million gallons of water. Or, to express it another way, Nelson [2] estimates that when using a dosage of

240 ppm of lime and assuming a figure of 15 per cent solids, there would be required 2 acre-feet of lagoon per year per million gallons of water softened.

The sludge produced in lime or lime-soda softening plants consists mainly of calcium carbonate and magnesium hydroxide, with much lesser amounts of silica and ferric and aluminum hydroxides. Table I presents the results of chemical analyses of sludge from three water softening plants.

TABLE I

CHEMICAL COMPOSITION OF DRY SLUDGE

Constituent	Per Cent by Weight		
	A	B	C
Silica (SiO_2)	0.90	0.67	1.75
Iron and aluminum oxides (R_2O_3)	0.56	0.78	1.01
Calcium oxide (CaO)	51.47	52.1	49.57
Magnesium oxide (MgO)	5.08	1.8	3.88
Carbon dioxide (CO_2)	41.99	43.8	38.94

A - Dayton, Ohio
B - Miami, Florida
C - Gainesville, Florida

The particle size of such sludge is extremely small. According to Sheen and Lammers,[3] the sludge produced by selective

lime softening (calcium only precipitated) has an average particle size of 5 - 7 microns. Black, [4] studying the sludge produced in the Miami plant found that 99 per cent had a particle size of 24 microns or less.

The percentage and physical character of the suspended solids are the factors determining sludge volume. Studies by Nelson [2] and experiences of the author indicate that the physical characteristics of water plant softening sludge vary widely. The concentration of sludge from softening basins may vary from 2 to 18 per cent by weight, depending upon the time and method of concentration in the softening process, the coagulant used, and the calcium-magnesium ratio of the raw water. More important than the percentage by weight of the solids in the sludge is the volume occupied by these solids. Black [4] shows that the increased magnesium content of the sludge decreases its settleability and increases the sludge volume.

The disposal of sludge from softening plants has been generally limited to either sludge lagoons or to watercourses. Lagooning has been satisfactory where adequate land areas are available. Discharge into watercourses is only allowable where no nuisance is created, and in this method of disposal, sludge banks must be periodically removed. Vacuum filtration, with disposal of

solids on land areas is also practiced. The discharge of water softening plant sludge into sanitary sewers is currently practiced at Gainesville, Daytona Beach, and Ocala, Florida. Sewage treatment plants at Daytona and Ocala utilize vacuum filtration of raw sewage sludge. Although softening plant sludge is of some value as a filter aid, odor problems at Ocala have required the construction of digesters. At Gainesville, although no difficulty in plant operation results from excess softening sludge in the sewage treatment process, sludge drying has been a problem. Normal sewage sludge requires about two weeks for drying, whereas the softening plant-sewage sludge mixture requires at least six weeks drying before removal. Additional digester capacity must be provided for the excess softening sludge volume.

Sheen and Lammers [3] describe the recovery of calcium carbonate from lime softening sludges produced at the Wright Aeronautical Company, Dayton, Ohio, softening plant. The raw water is treated with sufficient lime so that the softening reaction takes place at a pH of 9. 4, thereby selectively precipitating calcium carbonate, leaving the magnesium in solution. The softening sludge is then centrifuged and dried in a flash drying system. By this process, approximately 93 per cent of the calcium carbonate is recovered.

Recalcination of softening plant sludge is a process in which the sludge, concentrated in a centrifuge to 60 per cent solids, is burned at 2000°F, the calcium carbonate and magnesium hydroxide present being converted to the corresponding oxides. The greater percentage of the carbonate hardness present in natural waters is normally due to calcium bicarbonate, which is precipitated by either quick or hydrated lime. From the simple stoichiometric ratio obtained from the reaction:

$$CaO + Ca(HCO_3)_2 = 2\ CaCO_3 + H_2O$$

one pound of pure calcium oxide will theoretically produce 3.57 pounds of dry calcium carbonate sludge. In actual practice, this theoretical yield is never obtained due to impurities present in the lime and to the varying amounts of magnesium which are removed from the water. Both Nelson [2] and Swab [5] assume an average yield of 2.5 pounds of calcium carbonate sludge, dry basis, for each pound of commercial quicklime added.

Recalcination of calcium carbonate sludges has been practiced for many years in the pulp and paper industry. The economic success of the so-called "Kraft Process" requires this conversion in the recausticizing operation. However until recently this practice has not been applicable to the municipal softening field, due mainly to the low tonnages involved, and because the magnesium content of the sludge must be minimized.

Aultman [6] describes the pilot plant operation of recalcination of lime softening sludges produced from treatment of Colorado River water. Since the water to be treated contained 25 mg. /l. of magnesium, consideration was given to both the Hoover [7] and Lykken-Estabrook [8] processes, in order to produce a sludge of low magnesium content. The Hoover [7] process was used by Sheen and Lammers [3] in their work at the Wright Aeronautical plant. In the Lykken-Estabrook [8] process, sufficient lime is added to 12 per cent of the volume of water to be treated to soften the total volume of water. The sludge produced from this stage contains the magnesium present in the volume of water treated, and all the magnesium present in the reburned lime. The overtreated water from this first stage is then mixed with the remainder of the raw water, producing a sludge from the second stage of lower magnesium content.

Pedersen's [9] pilot plant work on recalcination of softening sludge at Marshalltown, Iowa, utilized a stationary flash drying calcining furnace. The lime produced by this method contained approximately 90 per cent calcium oxide, 4 per cent magnesium oxide and 5 per cent ferric oxide. The low magnesium and iron content of the finished product was due to removal each morning of the furnace coating containing these impurities.

Black et al [10] fully describe the recalcining operation at Miami, Florida. The sludge at Miami contains only 1.8 per cent MgO, therefore a very high quality quicklime containing 93 per cent CaO is produced.

In recent years, due to the increase in capacity of lime or lime-soda softening plants, the tonnages of softening sludge produced in a number of plants are sufficient to make recalcination feasible. The recalcination process is particularly attractive in areas where excessive freight rates increase the cost of delivered quicklime. At Miami, Black [10] indicates that with a total investment of approximately $800,000, there is a net profit of approximately $200,000 per year. A report [11] submitted to the Department of Water, City of Dayton, Ohio, recommending the construction of a $1,000,000 calcining plant, indicates a return on the investment of 17.3, 32.4, and 45.5 per cent when operating the plant at 50, 75, and 100 per cent of capacity, respectively. These very substantial savings are due both to the lower cost of quicklime produced from the recalcined sludge and to the fact that the recalcination process produces carbon dioxide in an amount far in excess of that required for the recarbonation of the softened water, thus eliminating the cost of the fuel presently used for that purpose.

The main problem of recalcination is the large quantities of magnesium in the softening plant sludge. At Miami, the magnesium content of the softening sludge is only 1.8 per cent. The magnesium content of most natural waters requiring softening results in sludges whose magnesium content is considerably higher than this value. The reduction in magnesium in the sludge has heretofore been obtained by either the Hoover [7] or Lykken-Estabrook [8] processes. However, when the Hoover [7] process is used for a water high in magnesium and only calcium is precipitated from the raw water, the hardness of the treated water will exceed the generally accepted value of 3 to 4 grains per gallon total hardness (as $CaCO_3$).

Sheen and Lammers [3], in their work at the Wright Aeronautical plant, found that centrifuging at 1000 times gravity refected approximately 50 per cent of the insolubles and magnesium. It must be borne in mind, however, that since the recalcined lime is reused in the softening process, a gradual "build-up" of magnesium will occur. An attempt is made to compensate for this build-up of magnesium in the reburned lime in the first stage of the Lykken-Estabrook [8] process.

In the recalcining operation, prior to centrifuging, the sludge from the softening tanks is first thickened to approximately 20 per cent by weight in a conventional sludge thickener. This is necessary

in order to economically obtain the required per cent recovery of solids in the centrifuging operation. Increasing amounts of bulky gelatinous magnesium hydroxide in the sludge to be thickened require a corresponding increase in area and volume of the thickener tank.

In 1946, the author suggested the dissolution of magnesium in softening plant sludge by the introduction of carbon dioxide contained in power plant stack gases. The purpose of this operation was to dissolve the magnesium hydroxide present in the softening plant sludge in order that it might be reprecipitated in a second stage softening operation to obtain adsorption of the silica present in the raw water. This process was entirely acceptable but no attempt was made to control the rate of carbonation. A similar non-controlled experiment was performed last year at the Gainesville, Florida water softening plant. Stack gas containing 11 per cent carbon dioxide was dispersed into softening plant sludge in order to determine whether the dissolution of magnesium from this sludge would result in better drying qualities of the softening plant-sewage plant mixture. Again excess gas was used and magnesium reductions as high as 80 per cent were obtained. The project was abandoned when no appreciable effects on the drying qualities of the water-sewage plant sludge mixture were obtained. In both of the above uncontrolled

experiments, the magnesium hydroxide in the softening plant sludge was greatly reduced in amount.

Of most importance to the recalcining operation is the work of Nelson [2] at the water softening plant at Findlay, Ohio. Nelson found that the carbonation of sludge prior to centrifuging reduces the magnesium content. With this magnesium reduction, a constant percentage of solids in the centrifuged cake is obtained at variable feed rates. However, the carbonation was not carried out under controlled conditions, the carbon dioxide being distributed through lawn sprayers into the sludge for 3 1/2 hours.

Evans and Hillary [12] conducted experiments on carbonation of magnesium hydroxide and dolomitic lime suspensions. By passing very large excesses of 100 per cent carbon dioxide gas at one atmosphere into magnesium hydroxide and dolomitic lime suspensions, a metastable solution of magnesium bicarbonate was formed in 15 minutes, having a concentration as MgO of 12 grams per liter. After thirty minutes carbonation, the concentration had decreased to the theoretical solubility of 8.6 grams per liter. Other metastable solutions containing magnesium bicarbonate in concentrations as high as 22 grams per liter as MgO were obtained. In the carbonation of calcined dolomite, metastable solutions of calcium bicarbonate were also formed. The authors state that the calcium goes into

solution prior to the magnesium but soon reaches a maximum and is then reprecipitated. It is not possible to predict from their data what would take place in the carbonation of water softening sludges composed largely of calcium carbonate and relatively low in both total solids and magnesium hydroxide.

The analysis of dry sludge produced at the Dayton, Ohio water softening plant was presented in Table I. Should this sludge be recalcined without preliminary treatment, the resulting lime would contain 92.1 per cent CaO and 7.9 per cent of insolubles and MgO. Since these impurities would tend to "build-up" in the recalcination process, and lower the quality of the lime produced, it is desirable, as part of the dewatering operation which must precede recalcination, to remove as much as possible of the silica, iron and aluminum oxides and magnesium hydroxide.

Six 55 gallon barrels containing concentrated water softening sludge from the Dayton, Ohio plant were shipped to the Bird Machine Company at Walpole, Massachusetts, in order that centrifuging tests could be made on the material to determine, first, the most economical size of centrifuge required for the 150 ton per day recalcining plant, and secondly to determine the effect of centrifuging on the impurities present. Table II presents the chemical analyses of sludge samples resulting from tests conducted by the

TABLE II

RESULTS OF CHEMICAL ANALYSES ON SLUDGE SAMPLES FROM DAYTON, OHIO

Sample	Per Cent Solids	Per Cent SiO_2 + Insol.	Per Cent R_2O_3	Per Cent CaO	Per Cent MgO
As Received	23.5	0.90	0.56	51.47	5.08
No. 1 Cake	55.3	0.65	0.43	52.60	3.33
No. 2 Cake	57.0	0.52	0.36	53.38	3.29
No. 3 Cake	59.0	0.43	0.33	52.90	3.14
No. 4 Cake	58.1	0.57	0.34	52.60	3.44
No. 5 Cake	56.8	0.53	0.36	51.98	3.82
No. 6 Cake	60.9	0.67	0.40	52.11	3.70
No. 7 Cake	60.3	0.89	0.37	52.30	3.30
No. 8 Cake	60.4	0.53	0.35	52.61	3.66
No. 9 Cake	59.3	0.46	0.29	52.40	3.85
No. 10 Cake	63.0	0.72	0.48	52.55	3.18
No. 1 Effluent	5.4	2.00	0.70	44.59	11.55
No. 2 Effluent	6.2	1.20	0.67	45.94	9.85
No. 3 Effluent	4.2	1.76	0.60	45.40	10.28
No. 4 Effluent	2.3	3.02	0.80	40.25	14.82
No. 5 Effluent	1.47	3.21	0.96	37.34	17.27
No. 6 Effluent	2.06	3.12	0.81	40.64	14.36
No. 7 Effluent	3.0	2.01	0.76	43.14	11.54
No. 8 Effluent	2.5	2.38	0.78	41.30	13.35
No. 9 Effluent	3.8	2.48	0.83	40.42	14.17
No. 10 Effluent	1.35	0.59	0.49	49.31	5.80
No. 1 Feed	16.3	0.89	0.48	50.94	4.62
No. 3 Feed	11.0	1.21	0.45	52.42	5.21
No. 5 Feed	8.3	0.56	0.50	48.25	5.43
No. 9 Feed	10.9	0.95	0.55	48.90	6.61
No. 10 Feed	10.5	0.53	0.40	52.26	3.26

Bird Company. These data indicate that approximately 50 per cent of the magnesium hydroxide and other insolubles are rejected by centrifuging. From other data submitted in the report from the Bird Company,[13] the following statements, in general, may be made with respect to the results to be obtained by centrifuging at approximately 1000 times gravity.

1. The percentage recovery of the cake is highest at low feed rates and decreases as input to the centrifuge is increased.
2. The percentage recovery in the cake is highest when the percentage of solids in the sludge is low, and decreases as sludge solids increase.
3. The percentage recovery increases as centrifuge speed is increased.
4. The composition of the cake is relatively constant over a wide range of operating conditions.

From these data, it was safe to assume that the Bird centrifuge operating with Dayton water softening sludge as feed, will recover 85 per cent solids at a cake moisture of 40 per cent and that the cake on a dry basis will contain a minimum of 52 per cent CaO. Softening the Dayton water to a final hardness of approximately 100 mg. /l. as calcium carbonate produces about 5600 pounds of dry

weight sludge suspended in about 204,000 pounds or 27,200 gallons of water. When operating at its designed capacity of 96 MGD, it will produce daily about 270 tons of dry weight sludge suspended in 2,600,000 gallons of water. This weight of sludge contains approximately 20 tons of magnesium hydroxide which must be removed as completely as possible without at the same time greatly reducing the amount of calcium carbonate recoverable for recalcining.

A 55 gallon drum of concentrated water softening sludge of the Dayton, Ohio plant was sent to the Dorr Company, Stamford, Connecticut, in order that tests might be conducted to determine the size of the sludge thickener. The sludge produced at the Dayton, Ohio water softening plant must be discharged at a rate of 3 million gallons per day. It averages 2.7 per cent solids by weight. The results of the Dorr Company [14] tests indicate that a thickener having a diameter of 167 feet would be required for thickening the raw sludge to 20 per cent by weight. From their past experience, the Dorr Company admitted that the thickener could be of much smaller area and volume except for its relatively high content of magnesium hydroxide.

To convert this magnesium hydroxide to soluble magnesium bicarbonate, 2 mols of carbon dioxide are required for each mol of magnesium hydroxide. Calculations indicate that only 30 tons per

day of carbon dioxide would be required to dissolve all of the magnesium hydroxide from the sludge produced when the Dayton plant is operating at maximum capacity. This is less than 20 per cent of the amount of carbon dioxide produced in the recalcination operation. However, the important factors establishing the feasibility of carbonating the sludge are the initial cost of the recarbonation basin and its pertinent equipment, the initial cost of the gas compressors, and their cost of operation when delivering gas containing 25 per cent carbon dioxide by volume. Offsetting these items to some extent would be the lower initial cost of the thickener required to partially dewater the sludge after carbonation and the higher quality of the lime produced.

The only published work on the carbonation of softening sludge is that of Nelson, (2) who recommended a 3 1/2 hour carbonation time. This would of itself render the process uneconomical. For example, assuming that the gas compressors will discharge against a 60 inch head of water and assuming an efficiency of 50 per cent, 52 brake horsepower is required to introduce into the recarbonation basin sufficient gas to convert all of the magnesium hydroxide into soluble magnesium bicarbonate when sludge is being discharged at the maximum rate of 3 MGD. To deliver five times the theoretical amount of carbon dioxide would

require 260 brake horsepower. It is obvious, therefore, that both carbonation time and the mol ratio of CO_2/MgO should be held to a minimum.

There are, therefore, a number of individual problems to be solved in connection with the successful and economical carbonation of water softening sludge. The first of these is to determine the percentage conversion of insoluble magnesium hydroxide to soluble magnesium bicarbonate at varying mol ratios of CO_2/MgO. The second is to determine the effect of retention time when other factors are held constant. The third is to determine the amount of calcium carbonate which would be dissolved under the conditions studied. Only after these three factors have been quantitatively evaluated can the economics of the process be determined.

CHAPTER II

EXPERIMENTAL PROCEDURE

The standard analytical procedure for the analysis of lime softening sludge is well-known. After removal of water, silica, and iron and aluminum oxides, calcium is precipitated as the oxalate and determined by titration with permanganate. Magnesium is usually determined by the pyrophosphate method. These latter determinations are not only extremely tedious and lengthy but the maximum accuracy of the magnesium determination is difficult to attain by even the skilled analyst. In view of the large number of determinations of both calcium and magnesium which this study would require, the use of versenate for determining these elements was explored. Because this method is relatively new and has been accepted only as a tentative one in the latest edition of "Standard Methods" [15] a brief discussion follows.

In 1947-48, Schwarzenbach [16] of the University of Zurich reported the results of a series of investigations of the complex ions of the alkaline earths and other metals with aminopoly-carboxylic acids. These acids and their soluble salts form very slightly ionized compounds with the alkaline earths, and the formation of such complexes can be employed for the determination of calcium, magnesium and other bivalent ions.

For determination of calcium and magnesium, an alkaline solution of the disodium salt of ethylenediaminetetraacetic acid, commercially known as "versene" and abbreviated H_4Ver, is used as the titrating agent. This determination of the total hardness due to both calcium and magnesium is based upon the formation of the stable, slightly ionized calcium and magnesium compounds:

$$Na_2\ H_2Ver + Ca^{++} + H_20 = Na_2\ CaVer + 2H_30^+$$

$$Na_2\ H_2Ver + Mg^{++} + H_20 = Na_2\ MgVer + 2H_30^+$$

Originally, Schwarzenbach [16] determined the end point of the reactions from pH changes resulting from the release of hydronium ions. Later, Biedermann [17] found that a dye, Eriochrome black T, the sodium salt of 1 - hydroxy, 2 - napthylazo, 5 - nitro, 2 - napthol, 4 - sulfonic acid, forms a soluble, undissociated wine-red compound with magnesium. Since this compound is ionized to a greater extent than the magnesium versenate compound, during the titration the versenate first combines with the free calcium ions, next with the free magnesium ions, and finally at the endpoint, extracts magnesium from the magnesium dye compound, changing the color from wine-red to blue.

For the versenate titration of total hardness, a pH value of about 10 is required, since above this value the magnesium is precipitated as the hydroxide, and below it, the magnesium is not

sufficiently bound to give the desired wine-red compound. A pH of 10 is maintained by the addition of sufficient amounts of ammonia - ammonium chloride buffer to the solution to be titrated.

Since this method gives no calcium endpoint, Rossum and Villarruz [18] suggested running a total versenate hardness, precipitating the calcium as the oxalate, then running a versenate titration on the remaining magnesium. Although this method would give the calcium concentration by difference, Schwarzenbach [19] produced another method. He found that the compound ammonium acid purpurate ($C_8H_4O_6N_5 \cdot NH_4H_2O$), or murexide, formed a colored complex with calcium but not with magnesium. Therefore, murexide can be employed for the determination of calcium hardness in the same manner as Eriochrome black T is employed for the determination of total hardness. Sodium hydroxide is first added to the sample to precipitate the magnesium and to attain the necessary pH. The color change at the endpoint is from pink to violet. Magnesium is therefore determined by difference.

Connors, [20] Diehl, Goetz, and Hasch, [21] and Betz and Noll [22] investigated the accuracy of the determination of calcium and magnesium by the versenate method. Three of their conclusions are of special interest. The first is that in determining

total hardness up to 100 ppm, the accuracy of the versenate method is equal to that of the gravimetric method for all ratios of calcium to magnesium. The second is that values of total hardness as high as 2000 ppm may be determined by versenate titration on undiluted samples. The third is that when titrating 25 ml. samples of waters containing magnesium hardness in excess of 500 ppm, error is introduced due to precipitation of magnesium as the hydroxide when the buffer solution is added. Since the magnesium concentration of many of the samples to be analyzed during this investigation would exceed this value, this point was given preliminary study. Two modifications of the standard procedure are possible and both were tried. One is obviously dilution of the sample before titration. The other is to add most of the versenate required for titration of the sample before addition of the buffer. Both were found to be effective in eliminating the error or in reducing it to very low values.

A second modification was required since the total hardness of some of the solutions to be analyzed was greater than 2000 ppm and excessive volumes of titrant would be needed if a versenate solution equivalent to 1 mg. $CaCO_3$ per milliliter were used. Accordingly, three standard versenate solutions were prepared as outlined in "Standard Methods" [15] such that 1 ml. equalled 5 mg., 10 mg. and 20 mg. total hardness as $CaCO_3$, respectively. A primary

standard was prepared by accurately weighing a dried sample of Bureau of Standards dolomitic lime, sample number 88, dissolving the sample in 6 M HCl, buffering to pH 10, and diluting to one liter.

Table III below presents results obtained when aliquots of this solution were titrated with each of three versenate solutions.

TABLE III

Total Hardness as $CaCO_3$	Titrating Solution 1 ml. equals 5 mg. $CaCO_3$	10 mg. $CaCO_3$	20 mg. $CaCO_3$
	mg. /l. as $CaCO_3$		
3125	3130	3125	3140
3125	3128	3122	3136
6250	6244	6260	6250
6250	6242	6258	6250
6250	6245	6252	6254

It was obvious from these results that versenate solutions several times more concentrated than normally used would yield data of sufficient accuracy for this study.

In order to ascertain whether or not versenate solution could be used to determine both the calcium and the magnesium content of samples of dried sludge, an approximately 0.4 g. sample

of Bureau of Standards dolomitic lime was accurately weighed, dissolved in a small excess of 6 N HCl, the solution diluted to almost one liter, buffered to pH 10 and further diluted to exactly one liter. Two milliliters of inhibitor solution was added to 50.00 ml. aliquots of the solution to precipitate the trace of iron present, and separate aliquot portion titrated to the total hardness endpoint and the calcium endpoint and magnesium determined by difference. The results are presented in Table IV. These data indicate that the method is of sufficient accuracy for many purposes when the mol concentrations of calcium oxide and magnesium are approximately the same.

TABLE IV

Sample No.	Bureau of Standards Analysis		Versenate Method	
	% CaO	% MgO	% CaO	% MgO
1.	30.49	21.48	30.62	21.37
2.	30.49	21.48	30.63	21.38
3.	30.49	21.48	30.40	21.80

However, when this method was used for the determination of the calcium and magnesium content of samples of water softening sludge, in which the concentration of calcium was many times that of the magnesium, inconsistent results were obtained. In order to eliminate this source of error, two ml. of 5 per cent ammonium oxalate solution was added to each 75.00 ml. aliquot, the solution

shaken thoroughly, allowed to stand for ten minutes, and then filtered through Whatman No. 40 filter paper. The first 15 ml. of filtrate was rejected and exactly 50.00 ml. collected and titrated with versenate in the usual manner. Employing this modification, results for magnesium concentration checked corresponding gravimetric data within 8 parts per thousand, as shown in Table V.

TABLE V
% MgO

Gravimetric Method	Versenate Method
3.80	3.77
3.25	3.23
3.25	3.28

The analytical procedure for the determination of the magnesium removed from the sludge by carbonation was as follows.

The per cent solids of raw sludge was determined by the usual method of accurately weighing a sample of raw sludge, drying the sample first on a steam bath, then in an oven at 110°C for one hour, and weighing. The dried sample was then thoroughly mixed in a mortar, redried, samples accurately weighed, dissolved in 6 M HCl, buffered, filtered, and the magnesium concentration determined by the versenate method after

precipitation of calcium as the oxalate. From these two procedures, the magnesium concentration of the sludge is determined.

After carbonation, the supernatant of the sludge was first filtered through Whatman No. 40 filter paper. A 50.00 ml. aliquot of the filtered supernatant was then titrated with versenate solution of which 1 ml. = 10 mg. combined calcium and magnesium as $CaCO_3$. Another 50.00 ml. aliquot was titrated with versenate solution of 1 ml. = 1 mg. for the determination of the calcium concentration. The magnesium concentration is obtained by difference. The per cent magnesium removal is determined as follows:

$$\frac{\text{Mg in supernatant of carbonated sludge} \quad \text{minus} \quad \text{Mg in supernatant of raw sludge}}{\text{Mg in raw sludge}} \times 100 = \% \text{ Mg removed}$$

LABORATORY EXPERIMENTS ON CARBONATION OF SLUDGE

The equipment used in the laboratory carbonation studies is presented in Plate 1. In these studies, the total volume of air - carbon dioxide mixture was 2 liters. The volume of the sample of raw sludge was 200 milliliters. The required volume of carbon dioxide for each experiment at one atmosphere and 25°C in the mixture was calculated from the concentration of magnesium in the raw sludge. Samples of raw sludge of known concentration were introduced into a cylinder, 3.4 cm. in diameter, containing a porous glass diffuser plate. To obtain the desired volume of air, clamps

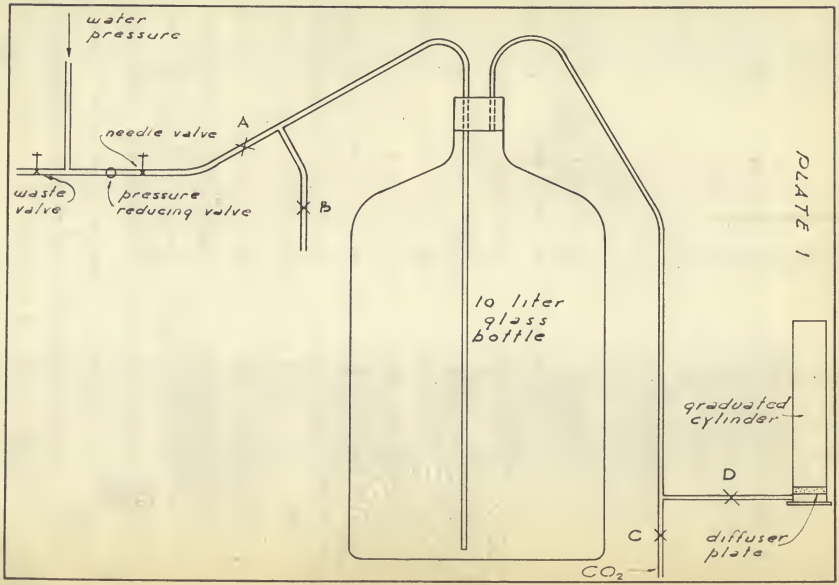
water pressure
needle valve
A
waste valve
pressure reducing valve
B
10 liter glass bottle
graduated cylinder
D
C
diffuser plate
CO_2

PLATE 1

B and D were opened and the required volume of water siphoned from the filled 10 liter glass bottle into a graduate. Clamps D and B were closed, B and C opened, and 100 per cent CO_2 introduced into the glass bottle, displacing the desired amount of previously CO_2 saturated water into a graduate. Clamps B and C were then closed and the glass container thoroughly shaken. The approximate time of carbonation was determined by collecting a volume of water at constant pressure into a graduate for a period of 5 minutes. Clamps A and D were then opened and the time required to refill the glass container with water accurately measured. As will be seen from subsequent data, this method was acceptable for the experiments performed.

The first experiments were designed to determine the effect of time of carbonation, with all other variables constant. The Gainesville sludge contained 4. 0% solids by weight, of which 3. 13% dry basis was MgO; the Dayton sludge contained 3. 2% solids by weight, of which 3. 33% dry basis was MgO. Throughout these experiments, the mol ratio CO_2/MgO was held at 3:1, or 1. 5 times theoretical requirement based on conversion of all of the MgO to the bicarbonate. The results of these tests are shown on Table VI and Plate 2.

TABLE VI

	% Solids	% MgO (dry basis)	mg. /l. Mg
Dayton Sludge	3.2	3.33	642
Gainesville Sludge	4.0	3.13	750

Volume of gas 2 liters
Volume of sample 200 milliliters
Mol ratio CO_2/MgO 3:1

GAINESVILLE SLUDGE		DAYTON SLUDGE	
Carbonation time in minutes	mg. /l. Mg in Supernatant of Carbonated Sludge	Carbonation time in minutes	mg. /l. in Supernatant of Carbonated Sludge
5.23	267	2.68	254
5.17	245	2.75	268
8.17	270	4.00	285
8.17	299	4.20	291
11.77	299	7.05	306
11.82	321	7.23	315
16.85	324	14.5	315
17.05	326	14.5	319
27.35	335	30.23	331
27.95	345	30.17	330

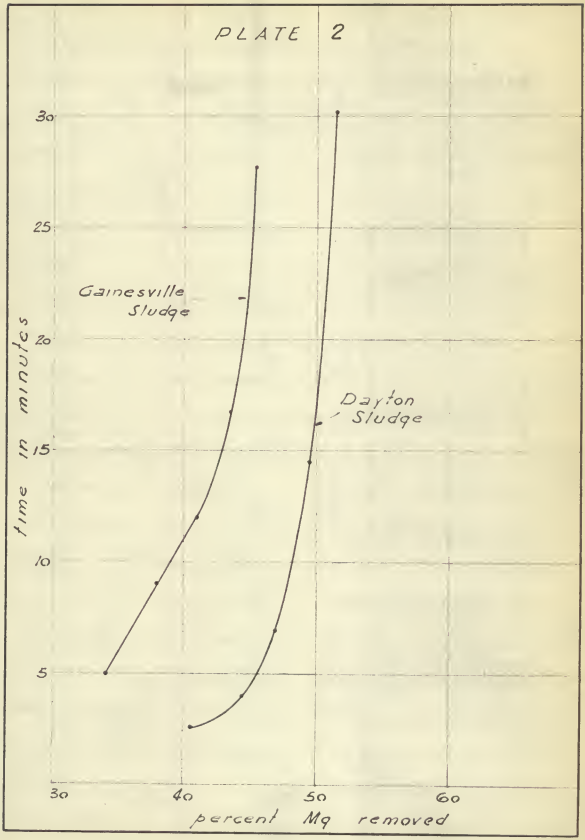
PLATE 2
30
25
20
15
10
5
time in minutes
Gainesville Sludge
Dayton Sludge
30
40
50
60
percent Mg removed

Table VI shows the results of duplicate runs for five different carbonation times on Gainesville sludge which varied from 5 - 20 minutes and of duplicate runs for five different carbonation times on Dayton sludge which varied from 3 - 30 minutes. Plate 2 presents the data in graphical form. On this plate, percentage of magnesium removed is plotted against time. The data indicate that conversion of the magnesium hydroxide to the soluble bicarbonate is very rapid, about 96 per cent of that removed from both the Gainesville and the Dayton sludges having been dissolved in the first 15 minutes.

The amount of MgO dissolved from the Gainesville sludge is somewhat less than that dissolved from the Dayton sludge, of approximately equal solids content, in any given time period. This may be due to the fact that at Gainesville, aluminum sulfate is being fed as a coagulant which would have the effect of substantially increasing particle size, whereas at Dayton, no coagulant is being used. Measurements of particle size of Dayton sludge by the Bird Company indicated that particle size ranged from 1 - 10 microns and averaged 3 - 4 microns.

In the second experiment, fresh sludge from the Gainesville softening plant was carbonated varying both carbonation time and mol ratio of CO_2/MgO. The data from these tests are presented in Plate 3. Carbonation times varied from 3.5 to 30 minutes and mol

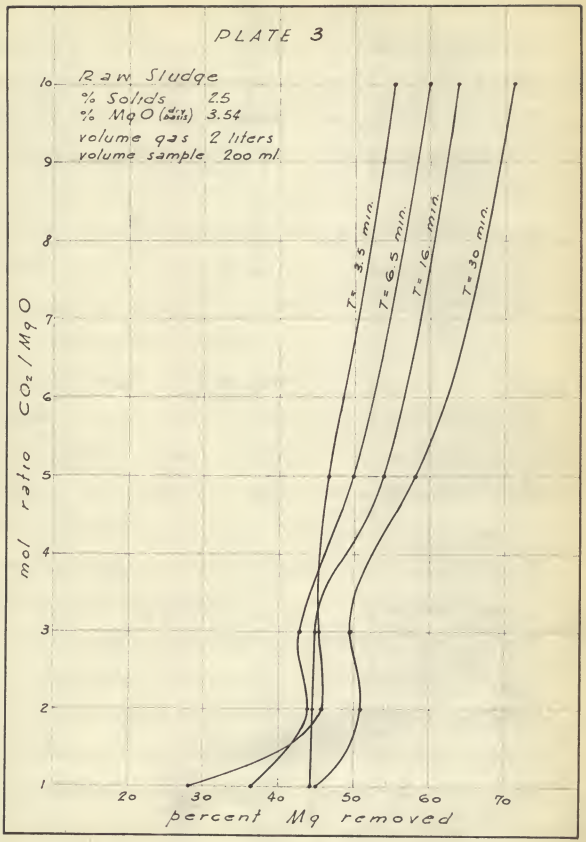
PLATE 3
Raw Sludge
% Solids 2.5
% MgO (as ash) 3.54
volume gas 2 liters
volume sample 200 ml
T = 3.5 min.
T = 6.5 min.
T = 16 min.
T = 30 min.
mol ratio CO2 / MgO
percent Mg removed
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70

ratio CO_2/MgO from 1 - 10. The curves show that in general, increasing the ratio CO_2/MgO exerts relatively little effect in converting MgO to the soluble bicarbonate. For example, for a 30-minute carbonation period, 45 per cent of the MgO present is dissolved at a mol ratio CO_2/MgO of 1:1, or 50 per cent of theoretical demand, whereas only 61 per cent is dissolved at a mol ratio CO_2/MgO of 10:1, or five times theoretical.

PILOT PLANT STUDIES OF CARBONATION OF SLUDGE

Recognizing that the laboratory experiments closely approximate maximum carbonation efficiency, a pilot plant was constructed adjacent to the solids-contact softening basin of the Gainesville water plant in order to secure data under actual operating conditions. This plant is shown in Plate 4. The carbonation tank had a volume of 500 gallons, a water depth of 4. 2 feet, and an area of 20 square feet. The manifold for introducing the carbon dioxide mixture consisted of four 2 inch pipes, each 4 feet in length with 1/4 inch orifices drilled on 3 inch centers. The gas for carbonation was obtained from the stack breeching of the power plant, scrubbed and compressed, and measured into the carbonation tank through a calibrated rotameter. The rate of flow of sludge in each experiment was calculated from the time required to fill a 10 gallon bucket with carbonation basin effluent. An Orsat test for

PLATE 4

PILOT PLANT

CARBONATION OF SOFTENING
PLANT SLUDGE

CO_2 was made on the stack gases hourly during the pilot plant experiments. The per cent by volume CO_2 was quite uniform, varying from 10.8 to 11.2. An average value of 11 per cent CO_2 by volume was used for all calculations.

In each experiment, 100 ml. aliquots of both raw and carbonated sludge were collected each five minutes for a period of one hour. If the retention time for the experiment was 30 minutes, collection of raw samples preceded that of the carbonated sludge by the retention time period. Aliquots of both raw and carbonated sludge so collected were composited, and the required analytical tests run.

Plate 5 shows the results of the first pilot plant run in which the mol ratio of CO_2/MgO was the variable. The diffuser was installed 4 feet below the water surface.

The inaccuracy of the rotameter at low gas flows set the minimum mol ratio CO_2/MgO at approximately 3:1 and the size of the compressor established a maximum mol ratio of CO_2/MgO. Plate 5 shows that between these ratios, the relationship between mol ratio CO_2/MgO and per cent MgO removed is linear. Reference to Plate 3 indicates that in laboratory runs, the relationship between the limiting values is also approximately linear, although in laboratory runs that is not true for mol ratios below 3:1.

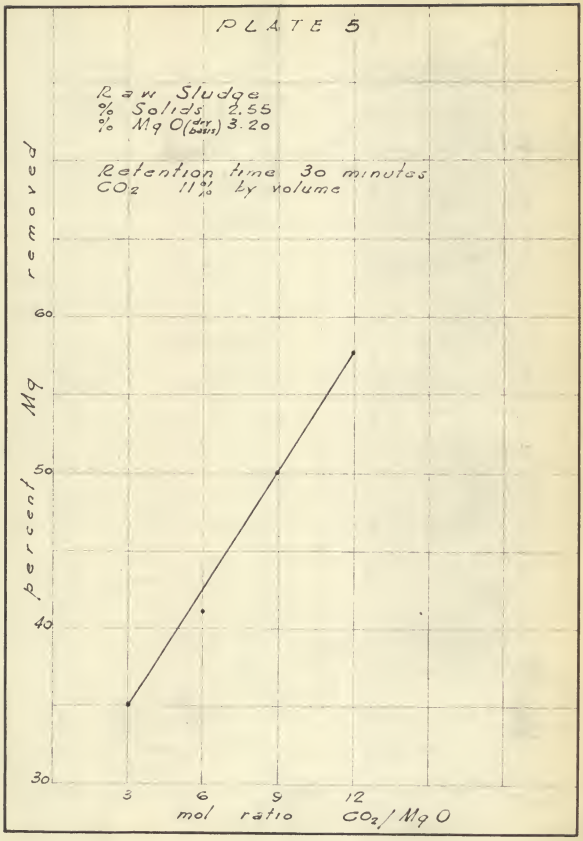
PLATE 5
Raw Sludge
% Solids 2.55
% MgO (dry basis) 3.20
Retention time 30 minutes
CO2 11% by volume
percent Mg removed
60
50
40
30
3
6
9
12
mol ratio CO2 / MgO

Comparison of Plates 3 and 5 also show that percentage removal of MgO was not as good in the pilot plant as in the laboratory experiments. This is believed to be due to the fact that in the laboratory diffuser, the gas bubbles were many times smaller than was the case in the pilot plant. There is no reason why percentage removal of MgO equal to those found in the laboratory could not be obtained in actual practice when more efficient diffusion of gas into the sludge is provided.

In order to carbonate the sludge at various CO_2/MgO mol ratios for low retention periods, the carbonation tank was modified. This was required because of the limited compressor capacity. The revision consisted of filling the tank to one-half its volume with river gravel. The CO_2 manifold was raised to within 2 feet of the liquid surface. The mol ratio of CO_2/MgO was between 2.2 and 9.6. Retention time was 7.5 and 15 minutes. The data obtained from these tests are presented in Plate 6.

Plate 6 shows the percentage removal is approximately linear between the limiting CO_2/MgO mol ratios. Comparison of Plates 5 and 6 shows that at any specific CO_2/MgO mol ratio, the per cent magnesium removal decreases with retention time.

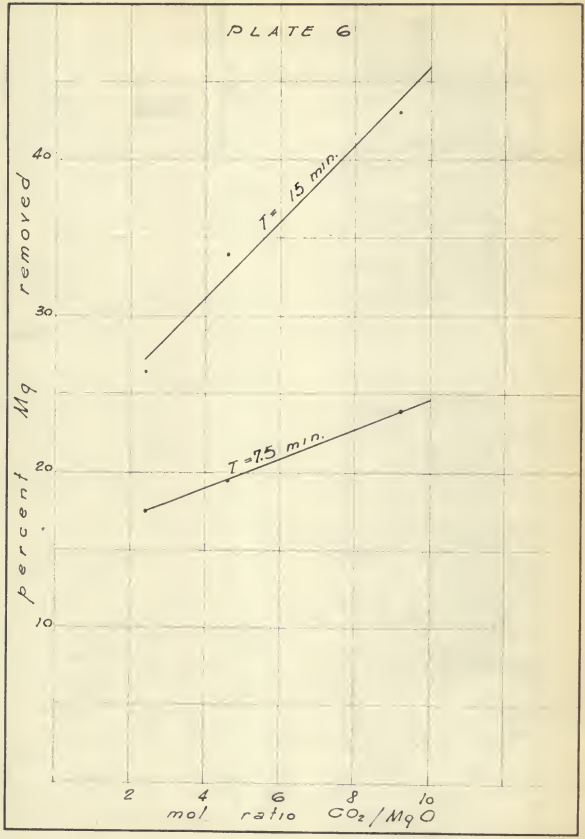
PLATE 6
percent Mg removed
40
30
20
10
T = 15 min.
T = 7.5 min.
2
4
6
8
10
mol ratio CO_2 / MgO

SETTLEABILITY TESTS

As previously stated, the settleability of the raw sludge is a function of the per cent solids by weight, the magnesium content, and the coagulant used in the softening process. Tests were conducted to determine the per cent volume occupied by the raw and carbonated sludge. These experiments were carried out in the carbonation basin at its maximum volume of 500 gallons and a grid depth of 4 feet. The concentration of the raw and carbonated sludge is presented in Table VII. The results of the settleability tests are presented in Plate 7.

These data indicate that the carbonation of sludge, with the conversion of part of the magnesium to the soluble bicarbonate, greatly reduces the volume occupied by the solids. It is evident from the data that the volume occupied by the solids in either the raw or carbonated sludge at the end of any period of settling depends upon the amount of magnesium hydroxide present, the volume decreasing with decreasing amounts of magnesium hydroxide. This effect is not so noticeable however in sludges of low solids content but it is to be noted that such sludges are not ordinarily obtained in the operation of lime or lime-soda softening plants.

The curves also indicate that maximum settling takes place and minimum sludge volumes are obtained in a relatively short time

TABLE VII

RAW SLUDGE

Run Number	mg. /l. Magnesium in Sludge	% by Volume 60 Minutes Settling
1.	841	75.5
2.	716	64.5
3.	403	29.0
4.	347	26.0
5.	418	38.0
6.	463	55.5
7.	539	57.0

CARBONATED SLUDGE

Run Number	mg. /l. Magnesium in Sludge	% by Volume 60 Minutes Settling
1.	659	30.5
2.	566	26.0
3.	202	13.0
4.	201	13.0
5.	201	12.0
6.	279	19.0
7.	289	17.7

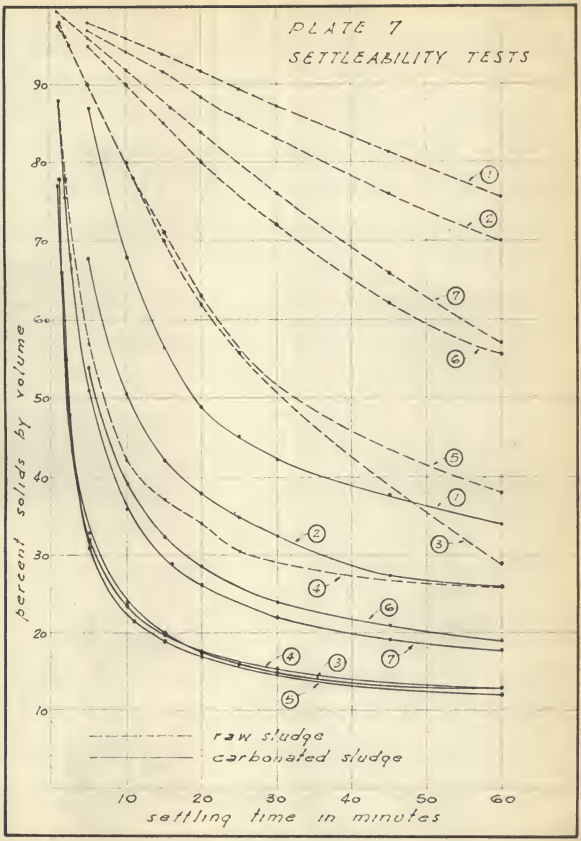
PLATE 7
SETTLEABILITY TESTS
percent solids by volume
90
80
70
60
50
40
30
20
10
raw sludge
carbonated sludge
10
20
30
40
50
60
settling time in minutes

in the case of carbonated sludges, whereas much longer times are required for raw sludges. These data made it possible to reduce the diameter of the thickener to be used at Dayton, Ohio from 167 feet to 132 feet, or from an effective area of 21,000 square feet to 13,000 square feet.

CALCIUM CARBONATE REMOVAL

Table VIII shows the amount of calcium carbonate dissolved in laboratory experiments with Gainesville sludge. The mol ratio CO_2/MgO was varied from 1:1 to 10:1, or from one-half to five times theoretical. Carbonation times were from 3.5 - 30 minutes. It will be noted that surprisingly little calcium carbonate is converted to the soluble bicarbonate. The raw sludge contained 34 mg./l. of dissolved calcium carbonate, due in part to supersaturation. Calcium bicarbonate in carbonated sludge varied from an average of 87 mg./l. for a 3.5 minute carbonation period to 103 mg./l. for a 30 minute carbonation period. The latter figure means that only 70 mg./l. of insoluble calcium carbonate was dissolved from approximately 36,000 mg./l. present, or about 0.2%.

Table IX presents corresponding data from laboratory tests on Dayton sludge. The percentage of calcium carbonate dissolved from this sludge is somewhat less than that dissolved from Gainesville sludge.

TABLE VIII

GAINESVILLE SLUDGE

$CaCO_3$ in Supernatant of Raw Sludge - 34 mg. /l.

Carbonation Time in Minutes	Mol/ratio CO_2/MgO	Ca as $CaCO_3$ in Supernatant Carbonated Sludge mg. /l.
3.5	1	90
3.5	2	89
3.5	3	83
3.5	5	86
3.5	10	86
		Average 87
6.5	1	76
6.5	2	116
6.5	3	86
6.5	5	84
6.5	10	84
		Average 89
16	1	83
16	2	106
16	3	108
16	5	86
16	10	82
		Average 93
30	1	100
30	2	102
30	3	96
30	5	101
30	10	114
		Average 103

TABLE IX

DAYTON SLUDGE

$CaCO_3$ in Supernatant of Raw Sludge - 24 mg. /l.
Mol Ratio CO_2/MgO - 3:1

Carbonation Time in Minutes	Ca as $CaCO_3$ in Supernatant of Carbonated Sludge - mg. /l.
2. 58	60
2. 75	64
4. 00	66
4. 20	66
7. 05	66
7. 23	68
14. 5	82
14. 5	80
30. 23	80

Table X presents data obtained in the pilot plant carbonation of Gainesville sludge. They show that approximately the same percentage of calcium carbonate was dissolved as was found in the laboratory tests.

TABLE X

GAINESVILLE SLUDGE
PILOT PLANT TESTS

Run Number	mg. /l. Ca as $CaCO_3$ in Supernatant of Sludge	
	Raw	Carbonated
1	18	22
2	20	26
3	18	24
4	18	95
5	13	86
6	22	39
7	17	70
8	20	74
9	22	66

CHAPTER III

DISCUSSION OF RESULTS

The fact that magnesium hydroxide can be selectively and fairly completely dissolved from water softening sludges containing much larger amounts of calcium carbonate is of great practical importance in many situations. The reason for its behavior in such situations is not clear and more than one factor may be involved.

The two reactions which are involved yield the same final product, the bicarbonate ion.

$$0\bar{H} + C0_2 = HC0_3^- \quad (1)$$

$$C0_3^{=} + C0_2 + H_20 = 2HC0_3^- \quad (2)$$

Using the solubility product of $Mg(0H)_2$ as 1.2×10^{-11}, the calculated pH value of its saturated solution is 10.36. Using the second dissociation constant of carbonic acid as 4.7×10^{-11}, and the solubility product of $CaC0_3$ as 4.82×10^{-9}, the calculated pH value of a saturated solution of $CaC0_3$ is 10.15. Many pH determinations using the glass electrode confirm the correctness of these data. If the reactions are looked upon as neutralization of a base by carbonic acid, the calculated pH values would slightly favor reaction (1).

Solubility does not appear to be a factor since the maximum concentrations of both the calcium and the magnesium ion were far

less than saturation values under the conditions of the experiment. Evans and Hillary [12] in their studies of the carbonation of aqueous suspensions of calcined magnesite or dolomite found that when the partial pressure of CO_2 was 3.85×10^{-4} atmosphere or 0.28 mm of Hg , the solubility of $Mg(OH)_2$, expressed as MgO, was 0.55 gm. /l. Of all supernatants from carbonated sludge analyzed during the entire study, only one exceeded this value for soluble magnesium, expressed as the oxide. However, Evans and Hillary [12] also found that upon further carbonation, metastable solutions were obtained containing as much as 22 gm. /l. of magnesium, expressed as MgO. This value is about 40 times greater than the highest value for soluble magnesium obtained in these studies. In like manner, the highest figure for soluble calcium, expressed as $CaCO_3$, found in any supernatant following carbonation was 125 mg. /l. The calcium alkalinity as $CaCO_3$ of natural waters may be several times this figure, and usually greatly exceeds the magnesium alkalinity.

A much more probable reason for the selectivity observed is to be found in the physical structures of the two insoluble components. Magnesium hydroxide exists as the coordination complex $Mg(H_2O)_4(OH)_2$ Because of the gelatinous and bulky nature of this compound, it is probable that the hydrated magnesium hydroxide formed in the softening reaction exists in the form of a polymer. The successive

acceptance by the hydroxyl group of protons from the carbonic acid would promote the dissolution of this compound.

Calcium carbonate does not exist as a coordination complex. In water softening sludges, it is a lyophobic crystalloid of extremely fine particle size. Having a sodium chloride crystal structure, the energy requirement for dissolution of this compound would be considerably greater than that required for dissolution of the magnesium hydroxide. By the above reasoning, one also may state that although both saturated solutions of $Mg(OH)_2$ and $CaCO_3$ have approximately the same pH value, $Mg(OH)_2$ is a considerably stronger base than is $CaCO_3$.

CHAPTER IV

SUMMARY AND CONCLUSIONS

A study has been made of the carbonation of the sludges obtained in softening the municipal water supplies of Gainesville, Florida and Dayton, Ohio by the lime-soda process. The volume concentrations of carbon dioxide have been limited to those of scrubbed stack gas and of the gas obtained by the recalcination of water softening sludge. The mol ratios of CO_2/MgO employed have been varied from 1:1, or 50 per cent of that required to convert all $Mg(OH)_2$ to the soluble bicarbonate to 10:1 or five times the theoretical requirement for complete conversion. Studies have been made both in the laboratory and in a pilot plant constructed especially for this work.

Because of the large number of determinations of both calcium and magnesium required, a study has been made of the volumetric method based upon titration with an aqueous solution of the disodium salt of ethylenediaminetetraacetate. Simple modifications have been found and used which have made it possible to employ versenate solutions such that 1 milliliter is equivalent to 10 milligrams of either calcium or magnesium expressed as calcium carbonate. These more concentrated solutions have been used with necessary

modifications for those analyses where high concentrations of calcium or magnesium, or both, were present.

It has been found that carbon dioxide in concentrations varying from 10 - 33 per cent by volume exhibits a high degree of selectivity in converting insoluble $Mg(OH)_2$ to the soluble bicarbonate in the presence of much greater amounts of finely divided $CaCO_3$. The following statements summarize the effect of the several variables which were studied.

1. Conversion of $Mg(OH)_2$ to the soluble bicarbonate is very rapid, about 96 per cent of that removed from the two sludges studied having been dissolved in the first 15 minutes.

2. The amount of $Mg(OH)_2$ dissolved is a function of the mol ratio of CO_2/MgO. The rate of solution of the $Mg(OH)_2$ increases rapidly up to a mol ratio of CO_2/MgO of 2:1. Beyond that point, as will be noted from the curves of Plates 3, 5 and 6, the relationship between the rate of solution of $Mg(OH)_2$ and the mol ratio of CO_2/MgO is linear.

3. Percentage removal of $Mg(OH)_2$ was not as great in the pilot plant as in laboratory experiments. This is

believed to be due to the fact that dispersion of the gas in the sludge suspension was much more efficient, and bubble size much smaller in the laboratory absorber than in the pilot plant.

4. The percentage of gelatinous, highly hydrated magnesium hydroxide in both raw and carbonate sludges is found to be the main factor determining their settleability and final volume after settling. Converting most of the insoluble $Mg(OH)_2$ to the soluble bicarbonate is found to greatly reduce the time of settling and the final volume of the settled sludge.

5. This selective action of carbon dioxide on sludges composed of mixtures of $Mg(OH)_2$ and $CaCO_3$ has a number of interesting and promising practical applications, both in water treatment, and in the treatment and disposal of industrial wastes.

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BIOGRAPHICAL NOTES

Frederic Arnold Eidsness was born on May 9, 1913 in Washington, D. C. and received all of his early schooling in the public schools of that city. He graduated from Washington Central High School in June 1931. In September 1931, he entered the College of William and Mary in Virginia, from which he received the degree of Bachelor of Science in chemistry in June 1936.

After graduation, he held employment as technical service representative of the Mathieson Chemical Company, Sanitary Engineer of the Florida State Board of Health, Division Engineer of Infilco, Inc., and at present is Vice-President of Black and Associates, Inc., Consulting Engineers, Gainesville, Florida.

He was registered as professional engineer in the State of Florida in July 1944. He is a member of the American Society of Civil Engineers, American Institute of Chemical Engineers, Florida Engineering Society, Federation of Sewage and Industrial Wastes Association, and the Florida Section, American Water Works Association of which he is a past chairman and received the George Warren Fuller Award in 1945. He is an officer of the Reserve Corps of the United States Public Health Service. He is the author of numerous papers in the field of water and sewerage.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

January 28, 1956

C. J. Byers
Dean, College of Arts and Sciences

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